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Energy Procedia 1 (2009) 1887–1894

Physics Procedia

www.elsevier.com/locate/procedia

GHGT-9

Reactive Transport Simulations to Study Groundwater Quality Changes in Response to CO_2 Leakage from Deep Geological Storage

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Abstract

As an effort to evaluate risks associated with geologic sequestration of CO_2, this work assesses the potential effects of CO_2 leakage on groundwater quality. Reactive transport simulations are performed to study the chemical evolution of aqueous Pb and As after the intrusion of CO_2 from a storage reservoir into a shallow confined groundwater resource. The simulations use mineralogies representative of shallow potable aquifers in the USA; both 2D (depth-averaged) and 3D simulations are conducted. Sensitivity studies are also conducted for variation in hydrological and geochemical conditions, as well as several other critical parameters. Model results suggest that a significant increase of aqueous lead (Pb) and arsenic (As) may occur in response to CO_2 intrusion, but in most sensitivity cases their concentrations remain below the EPA specified maximum contaminant levels (MCLs). Adsorption/desorption from mineral surfaces significantly impacts the mobilization of Pb and As. Results from the 3D model agree fairly well with the 2D model in cases where the rate of CO_2 intrusion is relatively small (so that the majority of CO_2 readily dissolves in the groundwater), whereas discrepancies between 2D and 3D models are observed when the CO_2 intrusion rate is comparably large.

Keywords: CO_2; Sequestration; Lead; Arsenic; Reactive transport; Groundwater

1. Introduction

One promising approach to reduce greenhouse gas emissions is injecting CO_2 into suitable geologic formations [1, 2]. Proper site selection and management of CO_2 storage projects will ensure that the risks to human health and the environment are low. However, a risk remains that CO_2 could migrate from a deep storage formation and arrive in shallow groundwater resources. The ingress of CO_2 will change the geochemical condition in the aquifer and will cause secondary effects mainly induced by changes in pH.

To date, the potential geochemical effects of CO_2 intrusion into USDWs have not been systematically assessed. Wang and Jaffe [3] conducted reactive-transport simulations considering the migration of CO_2 into an aquifer with

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doi:10.1016/j.egypro.2009.01.246

significant volume fraction of galena present as an essential mineral component. Their results suggest strongly increased lead concentration levels because of galena dissolution, in the case of a poorly buffered aquifer to levels higher than the maximum contaminant level (MCL) defined by the U.S. Environmental Protection Agency (EPA). It should be noted, however, that the authors intended their study as an illustrative example to demonstrate the potential effects of CO_2 intrusion on water quality. Their reactive-transport simulations do not necessarily represent realistic conditions expected to occur if CO_2 were to penetrate a potable aquifer, because very simplified geochemical systems were considered. Thus, while the simulation results of Wang and Jaffe [3] point to a potential concern that needs to be addressed, it is not clear how severe and widespread the problem would be in realistic cases.

This paper describes a systematic evaluation of the possible water quality changes in response to CO_2 intrusion into aquifers currently used as sources of potable water in the United States. Our goal is to understand, for a range of relevant aquifer conditions, the potential for hazardous constituents (such as heavy metals or arsenic) to be mobilized by the ingress of CO_2 and the distribution of these constituents in time and space. Ultimately, we need to determine the likelihood of drinking water standards to be exceeded. These issues are addressed by conducting reactive transport simulations for a variety of CO_2-release scenarios and aquifer conditions, which are based on a comprehensive geochemical model, developed utilizing a rigorous evaluation of more than 38,000 groundwater quality analyses from aquifers throughout the United States [4] .

2. Model Approach

2.1. TOUGHREACT Simulator

Modeling of CO_2 intrusion into shallow aquifers was conducted using the multiphase flow and reactive transport code TOUGHREACT [5]. This simulator was developed by introducing reactive chemistry into the existing framework of a non-isothermal multi-phase multi-component fluid and heat flow code [6]. A specific fluid property module for CO_2 sequestration includes a comprehensive description of the thermodynamics and thermophysical properties of a H_2O–NaCl-CO_2 system. For the conditions assumed in this study, the intrusion of gaseous CO_2 into a freshwater aquifer is modeled as two-phase flow system, with dissolution of CO_2 into water occurring instantaneously until equilibrium concentration is reached. Excess CO_2 migrates within the aquifer, driven mainly by buoyancy forces.

The geochemical model implemented in TOUGHREACT considers a variety of equilibrium and kinetic chemical reactions [5]. The thermodynamic data used have been derived from a comprehensive review of the published literature. Originally based on the equilibrium constants for aqueous species and minerals given in the EQ3/6 V7.2b data base [7], many substitutions and changes to this data base had been incorporated into TOUGHREACT over the years in response to revised or improved information on the given thermodynamic properties [5]. For kinetically controlled mineral dissolution and precipitation, a general form of rate law is used [8]. The TOUGHREACT version with the geochemical model and thermodynamic data base as described in Xu et al. [5] was the starting point for the modeling studies performed in this study. However, to adequately model the complex chemistry associated with the behavior of hazardous inorganic constituents in groundwaters, this data base needed to be significantly modified and expanded, as described in Birkholzer et al. [9]. Specific consideration was given to the thermodynamic data of the metal sulfide minerals and aqueous complexes as well as metal selenide minerals and aqueous complexes.

Adsorption via surface complexation has been widely studied [10,11] and is a key process with respect to the fate and transport of heavy metals [12] or other hazardous constituents such as arsenic [13,14]. We have therefore incorporated into TOUGHREACT a model considering adsorption via surface complexation. In this study, we consider goethite, illite, kaolinite, and smectite as principal adsorbents, mainly because these minerals have strong adsorption capacities with respect to lead and arsenic. A literature analysis was conducted to determine relevant surface complexation reactions and their thermodynamic constants for these cations and minerals.

2.2. Base Model Setup

The base model setup for most of the simulations presented here is depicted in Figure 1. The hydrogeological configuration is relatively simple. We consider a confined aquifer with a uniform vertical thickness of 10 m at a

reference depth of 50 m. The simulation domain comprises an area of this aquifer 500 m in length and 200 m in width. Water flows from left to right with a pore velocity of 10 m per year. Hydrogeologic properties are homogeneous and constant in time. CO_2 is assumed to migrate from a deeper geological storage site into the aquifer, representing, for example, local leakage through a fault zone. We assume in the base model a continuous CO_2 leakage rate of 7.5×10^{-5} kg/s, which corresponds to 2.36 tonnes per year, entering from below over an area of 100 m^2 (10 m × 10 m) at x = 105 m and y = 0 m. The simulation period is 100 years.

Background CO_2 partial pressure is set to 0.005 bar, which is a reasonable value for many aquifers in the United States [9]. Note that the base model assumes reducing conditions with a redox potential of approximately -0.23 V at pH around 7.6, defined by the coexistence of pyrite and goethite. The thermodynamic analysis of potable groundwater reported Apps et al. [4] has demonstrated that the majority of groundwater samples represent waters from reducing environments.

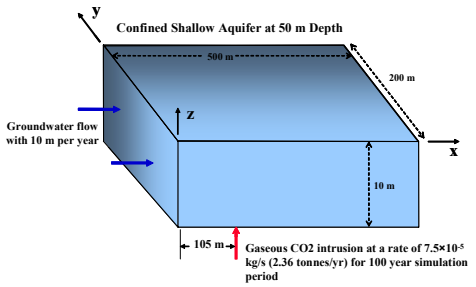

Figure 1. A schematic representation for the setup of reactive transport model.

3. Model Results

We focus in this study on the behavior of lead and arsenic as the hazardous constituents that may be mobilized by the intrusion of CO_2. The chemical reactions considered include aqueous complexation, mineral dissolution/precipitation, and adsorption/desorption via surface complexation. Solid solutions are not explicitly considered, while approximations are made in the current modeling work to offset the omission of an explicit solid solution model. All simulations were performed using a two-step procedure. First, initial equilibrium runs were conducted with a specified mineralogical composition to establish the initial (steady state) chemical composition of the groundwater at equilibrium condition with minerals and adsorbed matter before the intrusion of CO_2. Second, reactive transport simulations were conducted for the hydrogeological environment shown in Figure 1, with the initial aqueous chemical composition obtained from the initial equilibrium run. CO_2 intrusion starts at time zero and continues for the entire simulation period of 100 years.

3.1. Initial Geochemical Conditions for Base Model with Coastal Plain Sandstone

Several basic mineralogies were studied in a comprehensive sensitivity analysis, representing the conditions found in different regions of the country. Results are presented here for a mildly impure arenaceous sediment, referred to as Coastal Plain Sandstone aquifer. The basic mineralogy of this aquifer, including the hazardous-constituent-bearing minerals, is listed in Table 1. The selection of trace minerals containing hazardous metals as essential components was based on a study of thermodynamic controls in 38,000 groundwater quality analyses from the USGS National Water Information System (NWIS) Database. Their volume fractions were estimated from information supplied by the National Geochemical Survey (NGS) Database [9]. Table 2 shows the initial total aqueous concentration of major and hazardous inorganic constituents obtained from the initial equilibrium run. The calculated total aqueous Pb concentration is 1.3×10^{-9} mol/L, which corresponds to a local maximum in the histogram of measured Pb concentrations from the NWIS database for potable groundwater [4]. The calculated total aqueous As concentration is 4.42×10^{-8} mol/L, which falls close to the maximum frequency of As concentration

observed in NWIS analyses [4].

Table 1. Mineral volume fractions and possible secondary minerals,

Primary Mineral	Volume Fraction	Primary Mineral	Volume Fraction	Secondary Mineral
Quartz	0.77	Pyrite	0.00512	Dolomite
K-feldspar	0.0618	Calcite	0.0151	Magnesite
Oligoclase	0.06	Goethite	0.00601	Ankerite
Kaolinite	0.017	Arsenopyrite	9.05×10^{-6}	Dawsonite
Smectite-ca	0.0136	Galena	7.84×10^{-6}	Na-smectite
Illite	0.0285			Pyromorphite
Chlorite	0.0106			Ferroselite
Kerogen-os	2.67×10^{-3}			Clausthalite

Table 2. Initial total aqueous concentration of major constituents obtained by initial equilibrium run for Coastal Plain Sandstone.

Species	Ca	Mg	Na	K	Fe	Si	TIC	SO_4^{-2}	Cl	Pb	As	ionic strength
Concentration (mol/L)	9×10^{-4}	2.2×10^{-5}	2×10^{-3}	2.7×10^{-4}	5.6×10^{-6}	9.3×10^{-4}	3.3×10^{-3}	1.9×10^{-4}	2.1×10^{-4}	1.3×10^{-9}	4.4×10^{-8}	0.0051

3.2. 2D Model Results of Base Model

For the base case model (with a relatively small leakage rate), CO_2 dissolves almost instantaneously into the groundwater. A gas phase evolves after around 3 years close to the intrusion area, and a small two phase zone remains present during the remainder of the simulation period (Figure 2 left). The plume of elevated dissolved CO_2 which is given by total inorganic carbon (TIC) migrates primarily along the groundwater flow direction, while lateral spreading of dissolved CO_2 is minor (Figure 2 right).

The evolution of pH closely follows the evolution of TIC, with pH decreasing as the concentration of TIC rises. The lowest pH is around 5.87 outside of the two-phase zone, which is higher than the expected pH in a system without any buffering capacity. (For a non-buffered system, a pH around 4.5 would be expected). The moderation in pH decrease is caused primarily by the dissolution of calcite. The processes that control the changes in aqueous Pb and As concentration in response to CO_2 intrusion include desorption/adsorption, dissolution/precipitation of relevant minerals (galena for Pb and arsenopyrite in solid solution for As), and the dissociation/association of aqueous complexes. The resulting concentrations are furthermore affected by complex interaction between these processes.

Figure 3 (left) shows the total aqueous Pb concentration profile along the x-axis at y = 0 m for different times. The peak value of aqueous Pb is 3.4×10^{-8} mol/L in the small two-phase zone at the injection location after 5 years, which then decreases to 1.8×10^{-8} mol/L after 50 years. As time progresses, the peak moves incrementally downstream, and after 100 years falls to 1.6×10^{-8} mol/L. The aqueous Pb concentration downstream approaches a stable value around 1.1×10^{-8} mol/L (2.3 ppb). This value is significantly higher (about one order of magnitude) than the initial concentration, but remains below the MCL, which is 7.24×10^{-8} mol/L (15 ppb). Our results suggest that adsorption and desorption of Pb^{+2} ion from mineral surfaces are more important to the evolution of aqueous lead concentration than the precipitation /dissolution of galena. The ingress of CO_2 immediately disturbs both adsorption and solubility equilibria, but whereas adsorption reactions re-equilibrate very soon, the dissolution/precipitation of a hazardous mineral host is kinetically controlled and typically much slower. The relatively sudden release of Pb from adsorption sites increases the aqueous Pb concentration so significantly that the solution becomes in fact supersaturated with respect to galena (even though the groundwater becomes more acidic, suggesting a higher galena solubility) and galena precipitation occurs in the two-phase zone. The way that these processes—

desorption/adsorption and galena dissolution/precipitation—interact with each other is governed by the kinetic rate of galena dissolution/precipitation, the total sites of Pb on mineral surfaces, and the surface complexation constant.

Contrary to what is observed for Pb, desorption processes do not release sufficient arsenic into solution to inhibit the dissolution of arsenopyrite. Therefore, desorption of As from mineral surface and dissolution of arsenopyrite occur simultaneously and lead to a substantial increase of aqueous arsenic concentrations. The maximum concentration almost reaches the MCL (1.33×10^{-7} mol/L or 10 ppb) within the small two-phase zone, and is slightly lower (about 1.2×10^{-7} mol/L or 9 ppb) than the MCL within the elongated area of increased acidity downstream of the intrusion location (see Figure 3 right).

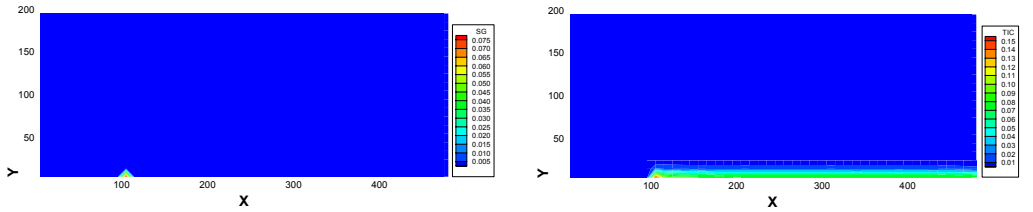

Figure 2. Spatial distribution of gas saturation degree (left) and total inorganic carbon (TIC) (right) after 100 years of intrusion

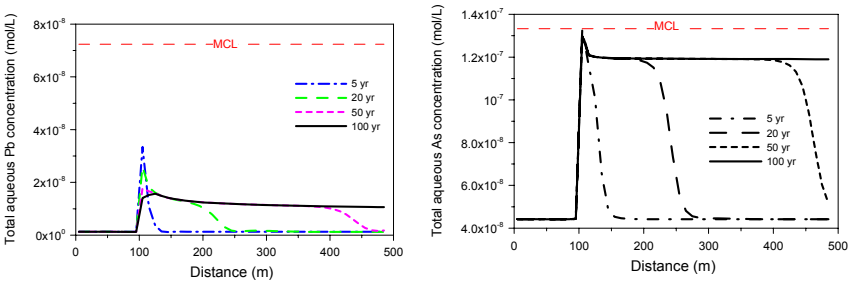

Figure 3. Total aqueous Pb (left) and As concentration (right) profile along x-axis at y = 0 m.

3.3. Sensitivity Analyses

A series of sensitivity analyses were conducted with respect to geochemical processes and parameters. Findings are briefly summarized here.

- In a simulation case without adsorption/desorption taken into account, the resulting long-term contamination of the aquifer is less significant near the region where CO_2 enters, whereas aqueous concentrations keep increasing with travel distance (eventually exceeding MCLs), as acidic water migrates further and more dissolution occurs.
- The relative importance of dissolution/precipitation versus adsorption/desorption is controlled by many factors including adsorption parameters and aquifer mineralogy, reaction kinetics, aqueous complexation processes, and solubility constants. For example, the role that adsorption/desorption plays in the mobilization of hazardous constituents depends highly on the total number of adsorption sites. A sensitivity run with lower site density reveals that early increases in aqueous lead and arsenic are much less significant, because desorption is less relevant in mobilizing contaminants.
- Changes in the solubilities of galena and arsenopyrite (by about a half order of magnitude) give rise to strong differences in the resulting aqueous concentrations of lead and arsenic. These differences result in part from the different dissolution behavior, but are also caused by changes in the adsorption/desorption characteristics.
- The initial volume fraction of galena was increased by three orders of magnitude in a sensitivity run to understand the consequences of natural variability in trace-element minerals. However, the changes in aqueous lead concentrations were negligibly small in this sensitivity case, mainly because lead mobilization is dominated

by desorption processes, not by galena dissolution. In contrast to what was observed for Pb, an increase of the arsenopyrite volume fraction (by two orders of magnitude) gives rise to a moderate increase in the aqueous As concentrations, mainly because the dissolution kinetics are assumed to change with a variation in the reactive surface area.

3.4. Three-Dimensional (3D) Simulation of CO_2 Intrusion

A two-dimensional depth-averaged model was used in all simulations described above. Thus, the vertical variation of gaseous and aqueous CO_2, as well as the vertical variation of the resulting geochemical changes, was neglected. This raises questions regarding the limitations of the 2D assumption. To answer such questions, a three-dimensional model was developed using the same model setup and similar model dimensions as in the 2D simulations. Like the 2D model, the 3D domain is 500 m long and has a uniform thickness of 10 m. However, the vertical extent of the model is now discretized using five model layers of 2 m thickness each. To increase computational efficiency, the lateral extent of the 3D model was reduced to 100 m, which was shown to be sufficient in the 2D simulations. CO_2 enters the model domain from below. Three simulation cases are considered here: The first one uses a model setup identical to the 2D base model described in Section 4.2, except that vertical variability is now considered. The second and third case are similar to the first case but with a reduced groundwater flow velocity and a higher CO_2 leakage rate, respectively. Note that in all cases, a confined aquifer has been assumed, so that gaseous CO_2 cannot escape into an overlying vadose zone.

3.4.1. Results from 3D Simulation of Base Model

Consistent with the 2D results described in Section 4.2, the two-phase zone predicted by the 3D model is relatively small. The plume of dissolved CO_2 and lower pH is elongated along the flow direction with limited lateral spreading, similar to what observed in 2D model. The spatial distribution of elevated As concentrations (Figure 4 left) corresponds to the area with lower pH. Comparison of predicted 3D and 2D results (see Figure 4 right) reveals that results from the depth-averaged 2D model are very similar to those predicted at the bottom and in the middle of the 3D domain.

3.4.2. Sensitivity to Groundwater Flow Velocity — 3D Model

Whereas the 2D and 3D models exhibit adequate similarity in the base model, they differ significantly when the groundwater flow rate decreases. A 3D simulation with groundwater flow rate equal to 1 m/y indicates that buoyancy forces are more relevant than in the base model and that gaseous CO_2 accumulates at the top of aquifer (Figure 5 left). Corresponding to spatial distribution of gaseous CO_2, spatial distributions of elevated dissolved CO_2, lower pH, and higher Pb and As concentration are characterized by the significant vertical variation and large lateral spreading at the top of aquifer. Figure 5 (right) shows the spatial distribution of As concentration as an example.

When the flow velocity decreases (while the CO_2 intrusion rate remains the same), the two-phase zone is enlarged; the area with elevated TIC is larger and TIC concentration is higher. Another consequence is that diffusion rather than just advection becomes important in controlling the transport of aqueous species. As a result, the plumes of elevated aqueous Pb and As concentrations move not only downstream with the groundwater flow but also in the upstream direction.

3.4.3. Sensitivity to CO_2 Leakage Rage-3D model

The increasing importance of buoyancy forces can also be seen when the CO_2 leakage rate increases as shown in Figure 6 (left). The plume of dissolved CO_2 is affected by both the distribution of gaseous CO_2 and the advective-diffusive transport of dissolved CO_2 with the groundwater flow. The dissolved CO_2 (TIC) concentrations therefore follow the general pattern of the CO_2 plume (e.g., the spreading of the plume at the top), but also show a significant migration of CO_2-charged water from the intrusion location further downstream. The spatial distributions of pH, total aqueous Pb, and total aqueous As concentration follow similar trends as TIC. Figure 6 (right) shows the spatial distribution of As concentration. When the CO_2 intrusion rate increases, we observe a much larger two-phase region and a correspondingly larger region with elevated TIC, Pb and As concentration, whereas the maximum Pb and As concentration is similar to what was observed in the case with a lower CO_2 intrusion rate.

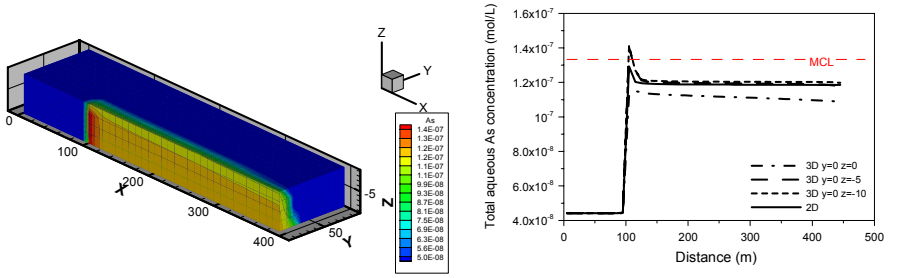

Figure 4. Spatial distribution of total aqueous As concentration after 100 years of CO_2 intrusion in 3D model with CO_2 leakage rate of 7.5×10^{-5} kg/s (left); Total aqueous As concentration along x-axis at y = 0 m and different aquifer depth (z = 0, -5 and 10 m) for 3D model and total aqueous As concentration along x-axis at y = 0 m for 2D model (right).

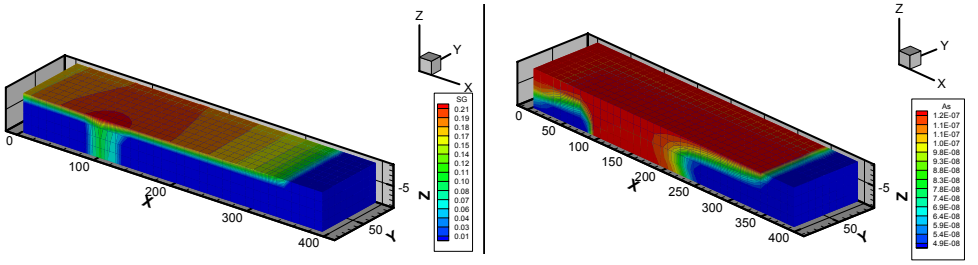

Figure 5. Spatial distribution of gas saturation degree (left) total aqueous As concentration (right) after 100 years of CO_2 intrusion in 3D model with groundwater flow rate equal to 1m/y.

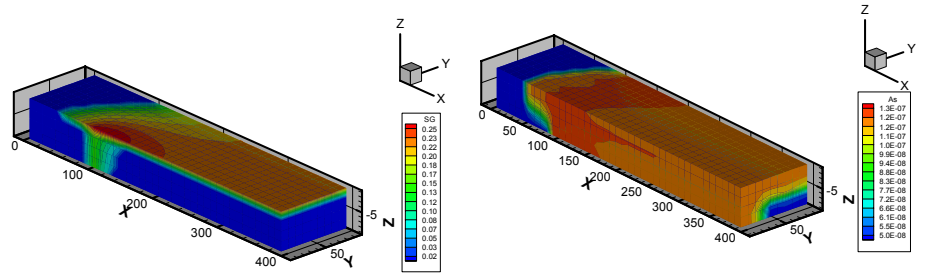

Figure 6. Spatial distribution of gas saturation degree (left) total aqueous As concentration (right) after 100 years of CO_2 intrusion in 3D model with CO_2 leakage rate equal to 6×10^{-4} kg/s.

4. Concluding remarks

Systematic reactive transport simulations have been conducted for a variety of CO_2-release scenarios to evaluate the effect of CO_2 intrusion into domestic shallow potable aquifers. Simulation results for the base model setup and implications of sensitivity studies are summarized as follows:

- Galena may precipitate or dissolve depending on the desorption characteristics of Pb, whereas desorption of As and dissolution of arsenopyrite occur simultaneously.

- Adsorption/desorption is arguably the most important process controlling the fate of hazardous constituents mobilized by CO_2 leakage. The relative importance of dissolution/precipitation versus desorption/adsorption is sensitive to many factors such as aquifer mineralogy, adsorption parameters, and kinetics of mineral dissolution.
- For a case with low groundwater velocity, the impact of CO_2 intrusion can be more significant but is also more localized.
- The rate of CO_2 entering an aquifer has only a minor effect on the maximum contaminant concentrations. Once the groundwater reaches its solubility limit, which occurs at relatively small intrusion rates, there is no further increase in total inorganic carbon and acidity. Consequently, no further mobilization of hazardous constituents occurs once local equilibrium has been achieved. Excess CO_2 remains in the gas phase and migrates elsewhere, thereby changing the spatial distribution of possible groundwater contamination, but the contamination level remaining essentially the same.
- Results from the 3D model agree fairly well with the 2D model in cases where the rate of CO_2 intrusion is relatively small. Discrepancies between 2D and 3D model are observed when the CO_2 intrusion rate is large enough to have a significant amount of gaseous CO_2 in the aquifer.

Acknowledgements

We thank the US Environmental Protection Agency, Office of Water and Office of Air and Radiation, for funding this study under an Interagency Agreement with the U.S. Department of Energy at the Lawrence Berkeley National Laboratory, Contract No. DE-AC02-05CH11231.

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